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13. ABSTRACT (Maximum 200 words) Our long-term objective is to develop two new concepts for molecular design of smart polymer surfaces: end functional surface active block copolymers to create smart surfaces with selective adhesion properties, and surfaces with properties that can be switched with light. In the former case, chain interpenetration, if present, does not contribute significantly to the interfacial energy release rate; adhesion enhancement is only observed when the copolymer terminus reacts with the adherend. Complementary to these studies, end-functional homopolymers are studied as model systems reflecting the character of all functional polymer surfaces. The lattice model we developed successfully reproduces functional polymer surface tensions, end group concentration depth profiles measured by angle dependant x-ray photoelectron spectroscopy (ADXPS), and surface structural changes accompanying surface reorganization. Two novel technologies have been developed that produce surfaces with chemical structures that can be switched upon illumination with light. Surface active block copolymers are employed to create surfaces with micropatterned carboxylic acid groups on polymeric substrates. End-functional azo compounds are used to produce chemically and physically patterned surfaces on gold substrates. In the latter case, surface functionality can be switched reversibly by photophysical induced conformational changes, while irreversible chemical changes can be achieved by photolysis reactions.			
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(4) Statement of the problem studied

The goal of this research project is to develop a fundamental scientific understanding of the behavior of functional polymer surfaces and to apply this knowledge toward the development of smart surfaces. The approach taken is to employ end-functional and center functional polymers as well as blends of end-functional and non-functional polymers as model systems through which to interrogate the surface properties of functional polymer systems in general. A number of such functional polymer systems are synthesized for this purpose, after which their surface structure and properties are characterized by a combination of contact angle analysis and angle-dependant x-ray photoelectron spectroscopy measurements. The experimental results are compared to theoretical lattice model calculations that allow for estimation of surface tensions and functional group concentration depth profiles for functional polymers of a wide variety of architectures. In the four different polymer systems studied, excellent agreement between experiment and theory are obtained when surface and bulk interaction parameters are estimated by group contribution methods. The lattice model provides near quantitative prediction of the surface properties of end- and center-functional polymers, and also accounts for the general behavior observed upon surface reorganization when functional polymers are placed in contact with water. The studies therefore provide a quantitative framework for the molecular design of functional polymer surfaces.

The principles learned in studying functional polymers are then applied to create several systems that comprise smart surfaces. Surface-active end-functional block copolymers are shown to be useful in delivering precise concentrations of functional groups to a surface and to impart selective adhesion properties. The effects of such surface modifiers on adhesion enhancement and adhesion hysteresis are also studied. Finally, several systems for modifying both hard and soft material interfaces are described that allow for changing the chemical structure of the surface simply by irradiation with an appropriate wavelength of light. The latter systems have enabled novel patterning strategies that can be applied directly to micropattern polymer surfaces with a variety of molecules such as organic dyes, micro- and nano-particles, and proteins.

(5) Summary of most important results

The most significant result of research performed under this grant is that we have now developed a highly advanced capability for the design of functional polymer surface properties at the molecular level. Through research funded by this grant, we have developed and now validated a theoretical approach that provides nearly quantitative predictions of both the surface structure and surface tension of functional polymers of essentially any linear architecture. This research has led to the establishment of three design principles that can be used to design surface modification molecules to fulfill the needs of specific polymer surface problems. The three principles for the design of functional polymer surfaces are: surface segregation in heterogeneous functional polymers, surface structure of functional polymers, and surface reorganization of functional polymer surfaces. The basis for and application of these principles was the subject of an invited *Highlight* article that recently appeared in the *Journal of Polymer Science*. The availability of molecular design principles for functional polymer surfaces has also led to the development of a number of applications ranging from adhesion promotion to surface patterning of biological molecules. A brief review of the major accomplishments is given below, where the reader is directed to the publications section for a list of the pertinent publications.

Surface structure and properties of functional polymers.

One of the enabling steps in the development of our surface design capability was the adaptation of the self-consistent mean field lattice model in order to treat functional polymer surfaces[1,2]. The lattice model was extended to treat essentially all cases of functional polymer architecture in the thesis of Patricia O'Rourke Muisener. These calculations show how to design polymer surfaces both for release and adhesive properties. The optimal architecture for release surfaces is to locate low surface tension functional groups at the chain ends. Adjacency of functional groups is a particular effective design feature. In the case of adhesive surfaces, we find that the optimal situation is to maximize the concentration of high energy reactive functional groups just below the surface. The optimal architecture to achieve this surface structure is a center functional chain with reactive functional groups located adjacently at the center of the polymer molecule. The results of the model have now been compared to experimental data for four polymer systems: end-functional polydimethyl siloxanes[1], end-fluorinated polystyrene and its blends with non-functional polystyrene[3,4], end-fluorinated polycaprolactone[5] and end-fluorinated and center-fluorinated polylactides[6]. Functional group concentration depth profiles and surface tension data for these systems agree quantitatively to the predictions of the lattice model, using only group contribution methods to estimate bulk and surface interaction parameters. We have also found that an adaptation of the model predicts qualitatively the surface reorganization that occurs when end-functional polystyrene surfaces are exposed to water vapor and are in the process of preparing a manuscript on this subject. As an illustration of an application of this research we demonstrated how end-fluorinated polystyrenes could be used as additives to control the dewetting of polystyrene thin films [7].

End-functional polymers have been used extensively as model systems for the investigation of surface properties of functional polymers. In the course of these studies we also discovered that end groups can effect bulk miscibility in polymer blends and have thus have published thorough investigations of end group effects on bulk properties for blends with both upper [8] and lower [9] critical solution temperature behavior.

Several review articles have been published on the design and properties of functional polymer surfaces[10, 11, 12].

Molecular Design of Smart Surfaces

The fundamental molecular design principles have been employed to develop concepts for the creation of smart surfaces. The first example is a surface-active end-functional block copolymer that imparted selective adhesion properties when adsorbed a polymer surface[13]. This research led to interactions with Dr. John Emerson from Sandia laboratories, where the PI has spent a least one month per summer for the past four years. The focus of this work is how functional polymer surfaces can be used to promote adhesion. We have shown that in most cases, hysteresis between silicone gels is the result of chemical reactions[14]. Of special interest is that the level of adhesion can be controlled by adjusting the length of the end-functional polymer brush molecules located at the surface[15]. A more recent study illustrate how residual functionality in the gels and interesting side reactions control adhesion at interfaces with silicone gels[16].

One of the difficulties in using end functional copolymers to functionalize polymer surfaces is that the molecules are very slow to diffuse to the surface from the bulk[17], therefore calling for some other processing technique to create smart surfaces. In a breakthrough study, we showed that typical surface active functional molecules can be delivered to the surface of a polymeric substrate using supercritical carbon dioxide[18].

A new thrust regarding smart surfaces was developed around the novel concept of using photoactive chemical groups to functionalize surfaces. The first demonstration of this principle was the development of photoactive self-assembled monolayers for the functionalization of gold. In the thesis of Feng Pan, in collaboration with a postdoctoral associate, Dr. Kwangjoo Lee, a series of trifluoromethyl and carboxylic acid terminated diazo compounds with terminal thiol functionality were synthesized. These materials were self-

assembled onto gold substrates, and studies have shown that their surface properties can be changed upon exposure to light[19,20]. We have also begun collaborating with Sandia National laboratories on extending this approach to create thin films of polymers on acoustic wave sensors for use in the detection of biological agents. The current technology suffers from dewetting of the polymer films when exposed to the agents. We attach photografting molecules to the surface to covalently attach the films and hopefully can solve this important problem.

Success in functionalizing and chemically patterning gold surface led to similar success in developing methods to do the same for polymeric substrates. One technique is based upon surface adsorption of surface active block copolymers that are subject to acid catalyzed photolysis[21]. When adsorbed at the surface, the low surface tension copolymer block spontaneously forms a nanometer thick surface layer. A photoacid generator is then added and the material is exposed through a mask. The impinging light causes formation of an acid that hydrolyzes the polymer to produce surface-bound carboxylic acid groups. The chemically patterned surface layer is therefore of the order of nanometers in thickness and is confined to the surface, leaving bulk properties unchanged. The carboxylic acid groups provide sites for grafting of cell adhesion ligands and other interesting biological compounds that form the basis of biosensor design. Because protecting groups for most chemical moieties are intrinsically low surface tension, protected groups tend to be soluble in supercritical carbon dioxide, and thus we have found the polymer surfaces can be functionalized with photoactive functional groups by delivering them with supercritical fluids. A patent disclosure has been filed on this invention[20].

The molecular designs we have developed for functionalizing polymer surfaces constitute families of macromolecular surfactants that we refer to as surface delivery vehicles. Surface delivery vehicles are all designed to be soluble in supercritical fluids, allowing for environmentally friendly processing onto substrate surfaces of arbitrary geometry, and to deliver precise surface concentrations of a number of interesting functional groups in spatially resolved surface patterns. Applications under study include the use of these techniques to fabricate surfaces decorated with biological molecules of interest for the fabrication of microarray sensors and bioinductive biomaterial surfaces.

(6) PUBLICATIONS

(a) Papers published in peer reviewed journals

1. "Segregation Dynamics of Block Copolymers to an Immiscible Polymer Blend Interface", D. Cho, C. Jalbert and J. T. Koberstein, *Macromolecules*, 33(14), 5245-5251 (2000).
2. "Tailoring Polymer Interfacial Properties by End Group Modification", J. T. Koberstein, in "Polymer Surface, Interfaces and Thin Films", "Series on Directions in Condensed Matter Physics, World Scientific Publishing, Singapore, pp115-181, 2000.
3. "Surface Energy and Surface Composition of End-Fluorinated Polystyrene", R. Mason, C. A. Jalbert, P. A. V. O'Rourke Muisener, J. T. Koberstein, J. F. Elman, T. E. Long and B. Gunesin, *Adv. Colloid Interface Sci.* 94(1-3), 1-19 (2001).
4. "The Effect of End Groups on Thermodynamics of Immiscible Polymer Blends. II Cloud Point Curves", Mark H. Lee, Cathy A. Fleischer, Ana Rita Morales, Jeffrey T. Koberstein and Ronald Koningsveld, *Polymer*, 42(21), 9163-9172 (2001).
5. "Polymer Surface Properties", J. T. Koberstein, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New York, 2001.
6. "The Effects of End Groups on Thermodynamics of Polymer Blends: 2. LCST Phase Diagrams", P. Schacht, J. T. Koberstein, *Polymer*, 43, 6527-6534 (2002).
7. "Optimal Chain Architectures for Polymer Surface Properties", P. O'Rourke-Muisener, S. Kumar and J. T. Koberstein, *Macromolecules*, 36,771-781 (2003).
8. "Surface Segregation in Miscible Blends of Polystyrene and Poly(vinylmethylether): Comparison of Theory and Experiment", C. Forrey, J. J. Koberstein, David Pan, *Interface Science*, 11(2), 211-223, 2003.

9. "Measurement and Modeling of End Group Concentration Depth Profiles for ω -Fluorosilane-terminated Polystyrene and its Blends", P. O'Rourke-Muisener, C. A. Jalbert, C. Yuan, J. Baetzold, R. Mason, D. Wong, Y. J. Kim, J. T. Koberstein, B. Gunesin, *Macromolecules*, 36 (8), 2956-2966, 2003.
10. "Morphology of Immiscible Polymer Blend Thin Films Prepared by Spin-Coating", P. Wang, J. Koberstein, *Macromolecules*, 37, 5671-5681, 2004.
11. "Molecular Design of Functional Polymer Surfaces", J. T. Koberstein, Highlight Article, *Journal of Polymer Science Polymer Physics Edition*, 42, 2942-2956, 2004. (Invited Submission)
12. "Adhesion Hysteresis in Polydimethylsiloxane gels" R. Mason, J. Emerson and J. T. Koberstein, *J. of Adhesion*, 80, 119-143, 2004.
13. "Photolithographic Technique for Direct Photochemical Modification and Chemical Micropatterning of Surfaces", K. Lee, F. Peng, G. T. Carroll, N. J. Turro and J. T. Koberstein, *Langmuir*, 20, 1812-1818, 2004.

(b) Papers presented in non-peer-reviewed journals or in conference proceedings

1. "Surface micropatterning of biomolecules through photolithography on block copolymer polymer brushes", Pan, F, Lee, K, Wang, P, et al *ABSTR PAP AM CHEM S* 225: 477-POLY Part 2 MAR 2003.
2. "Photogeneration and micropatterning of surface chemical groups using end functional azobenzene self-assembled monolayers", Lee, K, Pan, F, Carroll, GT, et al. *ABSTR PAP AM CHEM S* 226: 191-COLL Part 1 SEP 2003.
3. "Domain structures in the thin films of polystyrene / poly(tert-butyl acrylate) blends", Peng Wang, F. Pan, A. Wu, J. T. Koberstein, *ABSTR PAP AM CHEM S* 226: 78-PMSE Part 2 SEP 2003.

(c) Papers presented at meetings, but not published in conference proceedings

4. "Characterization of Polymer Surface Reorganization" International Conference on Polymer Characterization, Denton, TX, January 12, 2000. (Invited Presentation).
5. "Molecular Design of Functional Polymer Surfaces", P. O'Rourke and J. Koberstein, Adhesion Society, Hilton Head, Feb 22, 2000. (student won Distinguished Paper Award)
6. "Reorganization of Glassy Polymer Surfaces", American Physical Society, Minneapolis, MN, March 14, 2000.
7. "Surface Segregation in Miscible Binary Polymer Blends", J. Koberstein, C. Forrey and D. Pan, Materials Research Society, San Francisco, CA, April 26, 2000. (Invited Presentation).
8. "The Molecular Design of Bio-Inductive Polymer Surfaces", Gordon Conference on Adhesion, Tilton, NH, August 8, 2000.
9. "Biomaterials Surface Modification", Dawn A. Smith, Samuel J. Huang, and Jeffrey T. Koberstein, Amer. Chem. Soc. Poly Millenium 2000, Waikaloa, Hawaii, December 10, 2000.
10. "The Effect of End Group Modification on the Phase Behavior of Polymer Blends" Jeffrey T. Koberstein, M. Lee, C. A. Fleischer, P. Schacht and R. Konigsfeld, AIChE, Los Angeles, CA November 14, 2000.
11. "Molecular Design Concepts for Polymer Surfaces", ARCHIPOL, Mar del Plata Argentina, December 10, 2001. (Plenary Lecture).
12. "Enrichment and Reorganization of Functional Polymer Surfaces", 5th IPF Colloquium, Dresden Germany, November 15, 2002 (Invited Lecture).
13. "Bioinductive Biomaterials", Canadian Society for Biomaterials, May 2003, Montreal, Canada (Invited Plenary lecture).
14. "Molecular Design of Functional Substrates for Biological Applications", Columbia Symposium on Genomics, June 21, 2004.
15. "Molecular Design of Functional Polymer Surfaces", Gordon Conference on Adhesion, 2004. (invited lecture)

(d) Manuscripts submitted, but not published

1. "Adhesion Enhancement of Polymer Blend Interfaces by Reactive Block copolymer Brushes", W. Hu, H. R. Brown, J. T. Koberstein, R. Bhatia, J. P. Lingelser, Y. Gallot, Compte Rendus Chimie Academie des Science (Invited Submission).
2. "Surface Micropatterning of Biomolecules through Photolithography on Block Copolymer Polymer Brushes", F. Pan, P. Wang, K. Lee, A. Wu, N. J. Turro, J. T. Koberstein, Langmuir.
3. "Modification of Polymer Surfaces using Supercritical CO₂", D. Cho, J. T. Koberstein, Macromolecules.

(e) No technical reports have been submitted.

(7) Scientific personnel supported

1. Patricia O'Rourke Muisener, Department of Chemical Engineering, University of Connecticut, Ph.D. awarded March, 2001.
2. Ralf Mason, Polymer Program, University of Connecticut, Ph.D. awarded November, 2001.
3. Feng Pan, Department of Chemical Engineering, Columbia University, Ph.D. awarded, May 2003.
4. Peng Wang, Department of Chemical Engineering, Columbia University, Ph.D. awarded July, 2004.
5. Derek Wong, Polymer Program, University of Connecticut, Ph.D. awarded July, 2004.

(8) Inventions

"Micropatterning of Molecular Surfaces via Selective Irradiation"

(9) Bibliography

1. "End Group Effects on Surface Properties of Polymers: Semi-Empirical Calculations and Comparison to Experimental Surface Tensions for α,ω -Functional Poly(dimethyl siloxanes)", Claire Jalbert, Jeffrey T. Koberstein, Arvind Hariharan and Sanat K. Kumar, Macromolecules 30(15),4481-4490 (1997).
2. "Optimal Chain Architectures for Polymer Surface Properties", P. O'Rourke-Muisener, S. Kumar and J. T. Koberstein, Macromolecules, 36,771-781 (2003).
3. "Surface Energy and Surface Composition of End-Fluorinated Polystyrene", R. Mason, C. A. Jalbert, P. A. V. O'Rourke Muisener, J. T. Koberstein, J. F. Elman, T. E. Long and B. Gunesin, Adv. Colloid Interface Sci. 94(1-3), 1-19 (2001).
4. "Measurement and Modeling of End Group Concentration Depth Profiles for ω -Fluorosilane-terminated Polystyrene and its Blends", P. O'Rourke-Muisener, C. A. Jalbert, C. Yuan, J. Baetzold, R. Mason, D. Wong, Y. J. Kim, J. T. Koberstein, Binnure Gunesin, Macromolecules, 36 (8), 2956-2966, 2003.
5. Dawn Allison Smith, PhD Dissertation, University of Connecticut, 2001.
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12. "Molecular Design of Functional Polymer Surfaces", J. T. Koberstein, Highlight Article, Journal of Polymer Science Polymer Physics Edition, 42, 2942-2956, 2004. (Invited Article).

13. "Creating Smart Polymer Surfaces with Selective Adhesion Properties", J. T. Koberstein, D. E. Duch, W. Hu, T. J. Lenk, R. Bhatia, H. R. Brown, J.-P. Lingelser, and Y. Gallot, *J. Adhesion*, 66, 229-249 (1998).
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16. "The effects of Interfacial Reactions on Elastomer Adhesion", R. Mason, J. T. Koberstein, *J. Adhesion*, invited manuscript in preparation.
17. "Segregation Dynamics of Block Copolymers to an Immiscible Polymer Blend Interface", D. Cho, C. Jalbert and J. T. Koberstein, *Macromolecules*, 33(14), 5245-5251 (2000).
18. "Modification of Polymer Surfaces using Supercritical CO₂", D. Cho, J. T. Koberstein, *Macromolecules*, submitted for publication.
19. "Photolithographic Technique for Direct Photochemical Modification and Chemical Micropatterning of Surfaces", K. Lee, F. Peng, G. T. Carroll, N. J. Turro and J. T. Koberstein, *Langmuir*, 20, 1812-1818, 2004.
20. "Micropatterning of Molecular Surfaces via Selective Irradiation", patent pending.
21. "Surface Micropatterning of Biomolecules through Photolithography on Block Copolymer Polymer Brushes", F. Pan, P. Wang, K. Lee, A. Wu, N. J. Turro, J. T. Koberstein, *Langmuir*-submitted for publication.